Padé-approximant corrections to general variational expressions of scattering theory: Application to 5σ photoionization of carbon monoxide

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We discuss a method for systematically correcting results obtained using variational expressions in scattering theory. The approach taken is to compute a sequence of Padé approximants of the form $[N/N]$ for the error in an initial variational estimate obtained using a basis-set expansion. The relationship between the Padé-approximant approach and the iterative Schwinger method for correcting variational estimates is also examined. We discuss a large class of general variational expressions to which the Padé-approximant approach can be applied. The variational expressions considered include those for the wave function, for photoionization transition matrix elements, as well as for scattering matrix (K-matrix) elements. We have applied this approach to the 5σ photoionization of CO using the frozen-core Hartree-Fock and fixed-nuclei approximations. We find that the Padé-approximant method converges rapidly and reliably. Both total photoionization cross sections and photoelectron angular distributions from threshold to 40 eV are presented and compared to previous experimental and theoretical results. We find major quantitative discrepancies between the present results for the total cross section and previous theoretical results.

I. INTRODUCTION

The Hartree-Fock scattering equations for electron-molecule or electron—molecular-ion collisions, in the body-fixed frame and fixed-nuclei approximation, are of the form of simple three-dimensional potential-scattering equations. However, in addition to being nonspherically symmetric, the Hartree-Fock potential is also nonlocal. One common approach for solving these equations is to use single-center expansions, thus reducing the Hartree-Fock scattering equations to a set of coupled integro-differential equations for the radial scattering functions. Unfortunately, the solution of these equations for even small molecular systems containing a few heavy atoms (e.g., CO_2 and CO) can be very time consuming.[1] In the present paper, we describe a new procedure for solving the coupled-radial equations which is based upon the use of Padé approximants.[2]

Methods developed in the last several years for solving the single-center static-exchange equations include the noniterative static-exchange method of Raseev *et al.*,[3] the iterative static-exchange method of Collins *et al.*,[4] the iterative Schwinger variational method of Lucchese *et al.*,[5] the iterative $\tilde{C}$-functional method of Lee *et al.*,[6] the linear-algebraic method of Schneider and Collins,[7] and the separable exchange potential method of Rescigno and Orel.[8] The Padé-approximant approach described in the present study is a variational method which is related to the iterative Schwinger and $\tilde{C}$-functional variational methods. These variational methods have been successfully applied to several molecular systems, including e-H_2, e-LiH, and e-CO_2 scattering[5,9,10] as well as to the photoionization of H_2, N_2, NO, C_2H_2, and CO_2.[11–15]

The iterative Schwinger and $\tilde{C}$-functional methods consist of two distinct steps.[5] First a variational approximation to the matrix of interest (e.g., the K matrix) is computed using a trial wave function constructed from some initial basis set. Then the error in the initial, or "zeroth-order" approximation, is computed using an iterative procedure. When this method was first proposed[5] it was noted that the correction obtained after the first iteration could be written as a distorted-wave Schwinger-Born expression. As is well known,[2,16,17] such an expres-

sion is equivalent to the [1/1] Padé approximant to the distorted-wave Born series. The use of Padé approximants is an extremely useful approach to solving problems in scattering theory.[18,19] Thus a natural alternative to the original iterative Schwinger method is to compute a sequence of variational Padé approximants of the form $[N/N]$ to the error in the zeroth-order approximation. In the present paper, we give expressions for applying both the iterative Schwinger and Padé-approximant correction methods to a general class of inhomogeneous integral equations.

The Padé approximant and iterative Schwinger methods discussed here are approaches for correcting an initial variational estimate of a matrix element of the form $\langle R \mid \psi \rangle$, where ψ is the solution of the Lippmann-Schwinger equation and R is an arbitrary function. Variational expressions for matrix elements of the form $\langle R \mid \psi \rangle$, where R is general have been discussed in many places.[20–24] Several variational expressions specifically for the scattering matrix (e.g., K matrix) have also recently been discussed.[25–27] In this study we give a general expression for a large class of variational expressions for matrix elements of the form $\langle R \mid \psi \rangle$, based upon the Lippmann-Schwinger equation. Many of the expressions considered here have been studied before, and we will discuss the connections to earlier work. All of the variational expressions covered by the general relationship given here can be used as the starting point for the calculation of corrections using either the Padé-approximant or iterative Schwinger methods.

To compare the Padé-approximant method suggested here to the previously studied iterative Schwinger method we have computed cross sections for the 5σ photoionization of CO. This system has previously been studied theoretically using the multiple-scattering method (MSM)[28] by Davenport,[29] Wallace *et al.*,[30] and Stephens *et al.*,[31] and the Stieltjes-Tschebyscheff moment-theory approach (STMT) by Padial *et al.*[32] This photoionization cross section has not yet been studied using accurate single-center techniques. We find that the sequence of $[N/N]$ Padé approximants is generally more rapidly convergent than solutions obtained using the iterative Schwinger method. We have computed both total photoionization cross sections and photoelectron angular distributions, and compared them to the previous theoretical results[29,30,32] as well as to available experimental data.[33–35] We find significant quantitative differences in the total 5σ photoionization cross sections of CO between the present results and those of earlier studies.[29,32] In particular, we find that the peak in the experimental cross section at a photon energy of 24 eV (Ref. 34) is not well described by the present Hartree-Fock level results, in constrast to the STMT results of Padial *et al.*[32] We thus conclude that, in addition to the shape resonance which occurs in the $5\sigma \rightarrow k\sigma$ channel near 25 eV, there must be autoionization in the 5σ photoionization channel in the region of the photon energy of 24 eV.

II. PADÉ-APPROXIMANT AND ITERATIVE CORRECTION METHODS

A. Zeroth-order variational expression

The general problem we want to consider is the evaluation of a matrix element

$$M = \langle R \mid \psi \rangle , \tag{2.1}$$

where the function ψ satisfies the inhomogeneous equation

$$(1-K) \mid \psi \rangle = \mid S \rangle . \tag{2.2}$$

A variational estimate of the matrix element M can be obtained by first considering the Hermitian conjugate equation

$$\langle \chi \mid (1-K) = \langle R \mid . \tag{2.3}$$

We then have for the value of M

$$M = \langle R \mid \psi \rangle = \langle \chi \mid S \rangle = \langle \chi \mid (1-K) \mid \psi \rangle \tag{2.4}$$

and finally, using trial functions χ^t and ψ^t, we have the Schwinger-type variational expression for M given by[20,24]

$$M \sim M_0 = \langle R \mid \psi^t \rangle + \langle \chi^t \mid S \rangle - \langle \chi^t \mid (1-K) \mid \psi^t \rangle . \tag{2.5}$$

We now take the trial functions to be linear combinations of basis functions

$$\mid \psi^t \rangle = \sum_{u_i \in A_K} a_i \mid u_i \rangle , \tag{2.6a}$$

$$\langle \chi^t \mid = \sum_{v_i \in A_B} b_i \langle v_i \mid , \tag{2.6b}$$

where A_K is a ket basis set

$$A_K = \{ \mid \alpha_1 \rangle, \mid \alpha_2 \rangle, \ldots, \mid \alpha_\eta \rangle \} \tag{2.7a}$$

and A_B is a bra basis set

$$A_B = \{ \langle \beta_1 \mid, \langle \beta_2 \mid, \ldots, \langle \beta_\eta \mid \} . \tag{2.7b}$$

Requiring M_0 in Eq. (2.5) to be variationally stable with respect to the expansion coefficients leads to

$$\mid \psi^t \rangle = \sum_{\substack{u_i \in A_K \\ v_j \in A_B}} \mid u_i \rangle D_{ij}^{-1} \langle v_j \mid S \rangle \tag{2.8a}$$

and

$$\langle \chi^t | = \sum_{\substack{u_i \in A_K \\ v_j \in A_B}} \langle R | u_i \rangle D_{ij}^{-1} \langle v_j | \ , \tag{2.8b}$$

where D_{ij}^{-1} is the (i,j)th element of $\underline{D}^{-1}$, the inverse of the matrix $\underline{D}$ with elements

$$D_{ij} = \langle v_i | (1-K) | u_j \rangle \ . \tag{2.9}$$

Note that in order to satisfy the variational condition on M_0 we must compute both right and left inverses of the matrix $\underline{D}$, and thus $\underline{D}$ must be a square matrix. This fact forces us to have the same number of basis functions, η, in the sets A_K and A_B as indicated in Eqs. (2.7). The corresponding variational expression for M_0 is then

$$M_0 = \sum_{\substack{u_i \in A_K \\ v_j \in A_B}} \langle R | u_i \rangle D_{ij}^{-1} \langle v_j | S \rangle \tag{2.10}$$

or, defining the operator T as

$$T = \sum_{\substack{u_i \in A_K \\ v_j \in A_B}} | u_i \rangle D_{ij}^{-1} \langle v_j | \ , \tag{2.11}$$

we have again for M_0,

$$M_0 = \langle R | T | S \rangle \ . \tag{2.12}$$

B. Correction to variational expression

Now we want to derive an expression for M_c, which is the error in M_0, i.e.,

$$M_c = M - M_0 \ . \tag{2.13}$$

To do this we will follow the approach used in the iterative Schwinger method[5] and construct the zeroth-order solutions $| \psi_0 \rangle$ and $\langle \chi_0 |$ as

$$| \psi_0 \rangle = | S \rangle + K | \psi^t \rangle \tag{2.14a}$$

and

$$\langle \chi_0 | = \langle R | + \langle \chi^t | K \ . \tag{2.14b}$$

Then, using Eqs. (2.8) and (2.11), we get

$$| \psi_0 \rangle = (1+KT) | S \rangle \ , \tag{2.15a}$$

$$\langle \chi_0 | = \langle R | (1+TK) \ . \tag{2.15b}$$

Since the kernels in Eqs. (2.15) are separable, Eqs. (2.15) can be solved for $| S \rangle$ and $\langle R |$. Two useful identities are

$$T = P + PKT \tag{2.16a}$$

and

$$T = P + TKP \ , \tag{2.16b}$$

where

$$P = \sum_{\substack{u_i \in A_K \\ v_j \in A_B}} | u_i \rangle O_{ij}^{-1} \langle v_j | \tag{2.17}$$

and O_{ij}^{-1} is (i,j)th element of the inverse matrix, $\underline{O}^{-1}$, of matrix $\underline{O}$ with elements

$$O_{ij} = \langle v_i | u_j \rangle \ . \tag{2.18}$$

From Eqs. (2.16) it follows that

$$(1-KP)(1+KT) = (1+KT)(1-KP) = 1 \tag{2.19a}$$

and

$$(1+TK)(1-PK) = (1-PK)(1+TK) = 1 \ , \tag{2.19b}$$

and thus the operators in Eqs. (2.15) can be inverted to give

$$(1-KP) | \psi_0 \rangle = | S \rangle \tag{2.20a}$$

and

$$\langle \chi_0 | (1-PK) = \langle R | \ . \tag{2.20b}$$

Thus, as is the case with the iterative Schwinger method,[5] the zeroth-order solutions satisfy integral equations with separable kernels.[36] Now substituting Eqs. (2.20) into Eqs. (2.2) and (2.3), and using Eqs. (2.16) and (2.19) we get expressions for the exact wave functions in terms of the zeroth-order solutions,

$$[1-(K+KTK)(1-P)] | \psi \rangle = | \psi_0 \rangle \tag{2.21a}$$

and

$$\langle \chi | [1-(1-P)(K+KTK)] = \langle \chi_0 | \tag{2.21b}$$

or, to put Eq. (2.21b) into closer analogy to Eq. (2.3), we have

$$\langle \chi | (1-P)[1-(K+KTK)(1-P)] = \langle \chi_0 | (1-P) \ . \tag{2.21c}$$

It then follows that the error in M_0, defined as M_c in Eq. (2.13), is given by

$$\begin{aligned} M_c &= \langle \chi_0 | (1-P) | \psi \rangle = \langle \chi | (1-P) | \psi_0 \rangle \\ &= \langle \chi | (1-P)[1-(K+KTK)(1-P)] | \psi \rangle \ . \end{aligned} \tag{2.22}$$

Thus using Eqs. (2.21), and (2.22) we have a Born series for the correction matrix element M_c,

$$M_c = \langle \chi_0 | (1-P) | \psi_0 \rangle + \langle \chi_0 | (1-P)[(K+KTK)(1-P)] | \psi_0 \rangle + \cdots + \langle \chi_0 | (1-P)[(K+KTK)(1-P)]^n | \psi_0 \rangle + \cdots . \quad (2.23)$$

In this study we consider two different methods for computing M_c. The first method is to use a sequence of variationally stable Padé approximants to M_c based on the Born series given in Eq. (2.23). The second method is the iterative Schwinger method[5] which is based on the augmentation of the initial basis sets A_B and A_K with approximate solutions which transform Eqs. (2.15) into implicit equations for $|\psi\rangle$ and $\langle\chi|$. These equations can then be solved in an iterative fashion.

C. Padé-approximant method

Padé approximants of the type $[N/N]$ for matrix elements of the same form as M_c can be obtained using the Schwinger variational expression,[2,16,17] with the appropriate basis set. Thus for M_c we have the variational expression, in analogy to Eq. (2.5),

$$M_c \sim \langle \chi_0 | (1-P) | \psi'^t \rangle + \langle \chi'^t | (1-P) | \psi_0 \rangle - \langle \chi'^t | (1-P)[1-(K+KTK)(1-P)] | \psi'^t \rangle . \quad (2.24)$$

Then to obtain the $[N/N]$ Padé approximant we take ψ'^t to be a linear combination of the basis functions in the set B_K^N,

$$B_K^N = \{ |\psi_0\rangle, [(K+KTK)(1-P)] |\psi_0\rangle, \ldots, [(K+KTK)(1-P)]^{N-1} |\psi_0\rangle \} , \quad (2.25a)$$

and χ'^t to be a linear combination of the basis functions in the set B_B^N,

$$B_B^N = \{ \langle \chi_0 |, \langle \chi_0 | [(1-P)(K+KTK)], \ldots, \langle \chi_0 | [(1-P)(K+KTK)]^{N-1} \} . \quad (2.25b)$$

Then the variational expression for the exact matrix element M using the $[N/N]$ Padé approximation for M_c is

$$M_N^P = M_0 + \sum_{\substack{u_i \in B_K^N \\ v_j \in B_B^N}} \langle \chi_0 | (1-P) | u_i \rangle \times E_{ij}^{-1} \langle v_j | (1-P) | \psi_0 \rangle , \quad (2.26)$$

where E_{ij}^{-1} is the (i,j)th element of the inverse matrix, $\underline{E}^{-1}$, of matrix $\underline{E}$ with elements

$$E_{ij} = \langle v_i | (1-P)[1-(K+KTK)(1-P)] | u_j \rangle . \quad (2.27)$$

Although the general conditions under which the diagonal Padé sequence will converge are not known,[2] experience has shown that for problems of physical interest, paradiagonal Padé sequences are rapidly convergent.[18,19] It is of interest to note that Eq. (2.26) can be put into the form

$$M_N^P = \sum_{\substack{u_i \in A_K \cup B_K^N \\ v_i \in A_B \cup B_B^N}} \langle R | u_i \rangle D_{ij}^{-1} \langle v_j | S \rangle . \quad (2.28)$$

Thus the basis sets B_K^N and B_B^N can also be viewed as providing a systematic procedure for augmenting some initial basis sets A_K and A_B, which should lead to a convergent sequence of variational approximations to M.

D. Iterative Schwinger method

In Sec. IV C of this paper we will compare results obtained using the Padé method discussed above with the results from the iterative Schwinger method which has been discussed in detail elsewhere.[5] Briefly, at the Nth iteration of the iterative Schwinger method the matrix element M is given by

$$M_N^S = \sum_{\substack{u_i \in A_K \cup C_K^{N-1} \\ v_j \in A_B \cup C_B^{N-1}}} \langle R | u_i \rangle D_{ij}^{-1} \langle v_j | S \rangle , \quad (2.29)$$

where the augmentation basis sets C_K^N and C_B^N are defined as

$$C_K^N = \{ |\psi_N^S\rangle \} \quad (2.30a)$$

and

$$C_B^N = \{ \langle \chi_N^S | \} , \quad (2.30b)$$

and where

$$|\psi_N^S\rangle = |S\rangle + \sum_{\substack{u_i \in A_K \cup C_K^{N-1} \\ v_j \in A_B \cup C_B^{N-1}}} K |u_i\rangle D_{ij}^{-1} \langle v_j | S \rangle \quad (2.31a)$$

and

$$\langle \chi_N^S | = \langle R | + \sum_{\substack{u_i \in A_K \cup C_K^{N-1} \\ v_j \in A_B \cup C_B^{N-1}}} \langle R | u_i \rangle D_{ij}^{-1} \langle v_j | K , \quad (2.31b)$$

and where $|\psi_0^S\rangle$ and $\langle\chi_0^S|$ are given by $|\psi_0\rangle$ and $\langle\chi_0|$ of Eqs. (2.15).

Although the convergence of the iterative procedure defined by Eqs. (2.30) and (2.31) is not assured, this procedure does converge in many cases of interest.[9-15] When the iterative procedure does converge and the relations

$$D_{ij}^{-1}\langle v_j|S\rangle=\begin{cases}1, & \text{if } u_i\in C_K^{N-1}\\ 0, & \text{otherwise}\end{cases} \tag{2.32a}$$

and

$$\langle R|u_i\rangle D_{ij}^{-1}=\begin{cases}1, & \text{if } v_j\in C_B^{N-1}\\ 0, & \text{otherwise}\end{cases} \tag{2.32b}$$

are satisfied, then the converged functions ψ_N^S and χ_N^S are solutions of the original equations [Eqs. (2.2) and (2.3)], and M_N^S is exactly equal to M.[5]

The iterative Schwinger method[5] outlined above is related to a quasipotential approach discussed by Hahn and Luddy.[37] Specifically, Hahn and Luddy[37] examined the case where one takes the initial basis sets A_K and A_B to be null sets, and they state that this procedure can be unstable when the approximate functions ψ_N^S and χ_N^S change appreciably from one iteration to the next. Thus, for this iterative procedure to be generally useful, the inital basis sets must be large enough to give initial trial functions ψ_0 and χ_0 which are good approximations to the exact solutions.

Finally, we note that the $N=1$ results of the Padé and iterative methods are identical (i.e., $M_1^S=M_1^P$), but these methods will give different results for $N>1$.

III. VARIATIONAL PRINCIPLES IN SCATTERING THEORY

A. General expression

In this paper we will apply the methods discussed in Sec. II to the Lippmann-Schwinger equation of scattering theory, i.e., to

$$(1-G_0V)|\psi\rangle=|S\rangle\ . \tag{3.1}$$

The matrix elements which we want to compute are then

$$M(R,S)=\langle R|\psi\rangle\ . \tag{3.2}$$

It is often useful to partially expand ψ in the Born series and thus rewrite M as

$$M(R,S)=\sum_{k=0}^{n-1}\langle R|(G_0V)^k|S\rangle+I^n(R,S), \tag{3.3}$$

where $I^n(R,S)$ is given by

$$I^n(R,S)=\langle R|(G_0V)^n|\psi\rangle\ . \tag{3.4}$$

To calculate a variational expression for I^n we consider the Hermitian conjugate equation[20,24]

$$\langle\chi_n|(1-G_0V)=\langle R|(G_0V)^n\ . \tag{3.5}$$

The variational expression corresponding to Eq. (2.5) is then

$$I^n(R,S)\sim\langle R|(G_0V)^n|\psi^t\rangle+\langle\chi_n^t|S\rangle -\langle\chi_n^t|1-G_0V|\psi^t\rangle\ . \tag{3.6}$$

A large class of variational expressions can be constructed for I^n by considering expansion basis sets for χ_n^t and ψ^t of the form

$$A_K^{j,n}=\{(G_0,V)_{j-2n-1}|\alpha_k\rangle:\ k=1,2,\ldots,\eta\} \tag{3.7a}$$

and

$$A_B^i=\{\langle\alpha_k|[G_0,V]_i:\ k=1,2,\ldots,\eta\}\ , \tag{3.7b}$$

where the $\{\alpha_k\}$ is an arbitrary set of basis functions containing η elements, and the notation $(A,B)_i$ and $[A,B]_i$ is defined by

$$(A,B)_{2n}=(AB)^n\ , \tag{3.8a}$$

$$(A,B)_{2n+1}=(AB)^nA\ , \tag{3.8b}$$

and

$$[A,B]_n(A,B)_{-n}=1\ . \tag{3.9}$$

Using the basis sets defined in Eqs. (3.7) and the variational expression given in Eq. (2.10) we have, for I^n,

$$I^n\sim\sum_{k,l=1}^{\eta}\langle R|(G_0,V)_{j-1}|\alpha_k\rangle F_{kl}^{-1} \times\langle\alpha_l|[G_0,V]_i|S\rangle\ , \tag{3.10}$$

where F_{kl}^{-1} are elements of $\underline{F}^{-1}$, the inverse matrix of the matrix $\underline{F}$ with elements

$$F_{kl}=\langle\alpha_k|[G_0,V]_i(1-G_oV)(G_0,V)_{j-2n-1}|\alpha_l\rangle\ . \tag{3.11}$$

Then we can define $M_{ij}^n(R,S)$ as the variational approximation to $M(R,S)$ given by

$$M(R,S)\sim M_{ij}^n(R,S)=\sum_{m=0}^{n-1}\langle R|(G_0V)^m|S\rangle+\sum_{k,l=1}^{\eta}\langle R|(G_0,V)_{j-1}|\alpha_k\rangle F_{kl}^{-1}\langle\alpha_l|[G_0,V]_i|S\rangle\ . \tag{3.12}$$

B. Particular forms

Many of the variational functionals given by Eq. (3.12) have been discussed previously by other authors. In particular we note that $M^0_{11}(VS',S)$ is the Schwinger variational expression for the scattering matrix[38]:

$$M^0_{11}(VS',S) = \sum_{k,l} \langle S' \mid V \mid \alpha_k \rangle (V - V G_0 V)^{-1}_{kl} \langle \alpha_l \mid V \mid S \rangle \ , \tag{3.13}$$

where $(V - V G_0 V)^{-1}_{kl}$ are the elements of the inverse matrix of the matrix with elements $(V - V G_0 V)_{kl} = \langle \alpha_k \mid (V - V G_0 V) \mid \alpha_l \rangle$. Also, the four functionals F_1, F_2, F_3, and F_c discussed by Takatsuka and McKoy[25] are given by $M^1_{11}(VS',S)$, $M^1_{33}(VS',S)$, $M^1_{22}(VS',S)$, and $M^2_{33}(VS',S)$, respectively. Recently, Miraglia[26] examined a series of functionals $f^{(m)}_W$ which when applied to scattering without rearrangement are the same as the present $M^{m-2}_{2m-3,2m-3}(VS',S)$. Gross and Runge[27] have also analyzed functionals of this form, and their functionals $[f]_n$ are given by $M^n_{2n+1,2n+1}(VS',S)$.

These functionals can also be used to calculate matrix elements other than the scattering matrix. As Gerjuoy *et al.*[23] have pointed out, if $\langle R \mid$ is taken to be the coordinate eigenfunction $\langle \vec{r} \mid$, then $M^n_{ij}(\vec{r},S)$ becomes a variational functional for the wave function itself. Note specifically that for a particular $M^n_{ij}(R,S)$, the coordinate representation of the zeroth-order function, $\langle \vec{r} \mid \psi_0 \rangle$, used in the correction methods discussed in Sec. II and defined by Eq. (2.15a), is given by the variational functional $M^{n+1}_{i,j+2}(\vec{r},S)$. The $N=1$ results of the Padé or iterative methods will then be variational results obtained using variationally stable trial functions. The correction procedures outlined in Sec. II hence correspond to the use of supervariational principles which are also discussed by Gerjuoy *et al.*[23]

Finally, we will consider variational expressions for the dipole matrix elements, $\langle \phi \mid \vec{p} \mid \psi \rangle$, which are needed to compute photoionization cross sections. The function ϕ is a bound orbital of a molecular electronic wave function, $\vec{p}$ is either $\vec{r}$, which gives a dipole-length matrix element, or $E^{-1}\vec{\nabla}$, where E is the photon energy, which gives a dipole-velocity matrix element, and ψ is now the photoelectron continuum orbital for the photoelectron. In previous papers,[11–15] the present authors have used, in conjunction with the iterative Schwinger method, the variational expression

$$M^1_{13}(\vec{p}\phi,S) = \langle \phi \mid \vec{p} \mid S \rangle + \sum_{k,l} \langle \phi \mid \vec{p} G_0 V \mid \alpha_k \rangle (V - V G_0 V)^{-1}_{kl} \langle \alpha_l \mid V \mid S \rangle \tag{3.14}$$

to compute these dipole matrix elements. The expansion basis sets that were used there were those obtained by iteratively correcting the variational expression $M^0_{11}(VS',S)$ for the scattering matrix and not those that would have been obtained by directly correcting Eq. (3.14). The fact that the dipole matrix elements computed in those studies were variationally stable, was not recognized at that time. In Sec. IV we will consider the functional $M^3_{35}(\vec{p}\phi,S)$ which is related to the $\tilde{C}$ functional, F_C which in the present notation is given by

$$M^2_{33}(VS',S) = \langle S' \mid V \mid S \rangle + \langle S' \mid V G_0 V \mid S \rangle + \sum_{k,l} \langle S' \mid V G_0 V \mid \alpha_k \rangle (V - V G_0 V)^{-1}_{kl} \times \langle \alpha_l \mid V G_0 V \mid S \rangle \ . \tag{3.15}$$

This functional was first suggested by Takatsuka and McKoy[25] and has been applied by Lee *et al.*[6] The explicit expression for M^3_{35} is

$$M^3_{35}(\vec{p}\phi,S) = \langle \phi \mid \vec{p} \mid S \rangle + \langle \phi \mid \vec{p} G_0 V \mid S \rangle + \langle \phi \mid \vec{p} G_0 V G_0 V \mid S \rangle + \sum_{k,l} \langle \phi \mid \vec{p} G_0 V G_0 V \mid \alpha_k \rangle (V - V G_0 V)^{-1}_{kl} \langle \alpha_l \mid V G_0 V \mid S \rangle \ . \tag{3.16}$$

IV. APPLICATION TO 5σ PHOTOIONIZATION OF CO

A. Scattering potential

We will demonstrate the usefulness of the Padé-approximant correction method and compare it to the iterative Schwinger method by studying the 5σ photoionization of CO at the Hartree-Fock level. This cross section contains a shape resonant feature in the $5\sigma \rightarrow k\sigma$ channel.[29] We chose this example because it was found to be a relatively difficult case to apply the iterative Schwinger method to, and, moreover, accurate HF level results for the 5σ pho-

toionization of CO have not been previously published.

In the present study we have computed the 5σ photoionization cross section of CO in the fixed-nuclei and frozen-core—Hartree-Fock[39] (FCHF) approximations. Both the dipole-length and dipole-velocity forms of the cross section are obtained. In a previous study of the isoelectronic system N_2,[12] we found that the length and velocity forms of the cross section straddled the experimental results except in spectral regions where autoionization effects were important.

The target wave function was taken to be the Hartree-Fock wave function of McLean and Yoshimine[40] with the internuclear separation $2.132a_0$. All required matrix elements were computed using single-center expansion techniques. Detailed discussions of the numerical methods used have been given elsewhere.[12,41] We have performed the single-center expansions about the center of mass of the molecule. The expansion parameters for the scattering potential were based upon experience obtained in the N_2 study,[12] and are as follows:

(1) $l_m=29$, maximum l included in the expansion of scattering functions;

(2) $l_s^{\rm ex}=29$, maximum l included in the expansion of the scattering functions in the exchange terms;

(3) $l_i^{\rm ex}=16(1\sigma)$, $16(2\sigma)$, $8(3\sigma)$, $6(4\sigma)$, $5(5\sigma)$, and $5(1\pi)$, maximum l included in the expansion of the occupied orbitals in the exchange terms;

(4) $l_i^{\rm dir}=29$, maximum l included in the expansion of the occupied orbitals in the direct potential;

(5) $\lambda_m^{\rm ex}=29$, maximum l included in the expansion of $1/r_{12}$ in the exchange terms;

(6) $\lambda_m^{\rm dir}=58$, maximum l included in the expansion of $1/r_{12}$ in the direct potential (including the nuclear potential terms);

(7) $l_p=7$, maximum l included in the expansion of the scattering solution [defined by Eq. (7) of Ref. 12].

From the more detailed convergence studies performed on N_2,[12] we expect that the expansion parameters used here should give cross sections accurate to better than 5% and should reproduce the peak position of the resonant cross sections in these systems to better than 0.5 eV. The radial expansion grid contained 1000 points extending out to $r=100a_0$ with the smallest step size of $0.01a_0$ used from the origin to $r=2a_0$ and the largest step size being $0.16a_0$.

For the 5σ photoionization of CO we have two continuum symmetries, $k\sigma$ and $k\pi$. The initial basis sets $\{\alpha_k\}$ used in Eqs. (3.7) for these two scattering symmetries are given in Table I. These basis sets are composed of spherical Gaussian functions,[10] defined by

$$\alpha^{\gamma,l,m,\vec{A}}(\vec{r}) = N_{\gamma lm}\,|\vec{r}-\vec{A}|^{l} e^{-\gamma|\vec{r}-\vec{A}|^2} Y_{lm}(\Omega_{\vec{r}-\vec{A}})\,. \quad (4.1)$$

TABLE I. Scattering basis sets used in variational expressions. These basis sets are composed of spherical Gaussian functions as defined in Eq. (4.1) of the text.

Center[a] ($\vec{A}$)	l	m	Exponents (γ)
	$5\sigma\rightarrow k\sigma$		
C	0	0	10.0, 4.0, 1.6, 0.63, 0.25, 0.1
C	1	0	1.0, 0.32, 0.1
O	0	0	10.0, 4.0, 1.6, 0.63, 0.25, 0.1
O	1	0	1.0, 0.32, 0.1
c.m.	0	0	4.0, 1.6, 0.63, 0.25, 0.1
c.m.	1	0	1.0, 0.32, 0.1
c.m.	2	0	0.32, 0.1
	$5\sigma\rightarrow k\pi$		
C	1	1	4.0, 1.6, 0.63, 0.25, 0.1
C	2	1	0.32, 0.1
O	1	1	4.0, 1.6, 0.63, 0.25, 0.1
O	2	1	0.32, 0.1
c.m.	1	1	1.0, 0.32, 0.1
c.m.	2	1	0.32, 0.1
c.m.	3	1	0.1

[a]c.m. denotes a function at the center of mass.

B. Computational approach

The matrix elements needed to compute the photoionization cross section are[12]

$$I_{lm\mu}=k^{1/2}\langle\phi\,|\,p_\mu\,|\,\psi^{(-)}_{klm}\rangle\ , \tag{4.2}$$

where k is the photoelectron momentum and $\psi^{(-)}_{klm}$ is the partial-wave solution whose *out-state* is described by the quantum numbers l and m.[42] Alternatively to using the out-state wave function one can use the standing-wave solutions $\psi^{(P)}_{klm}$ through the relation[43]

$$\psi^{(-)}_{klm}(\vec{r})=e^{i\sigma_l}\sum_{l'}\psi^{(P)}_{kl'm}(\vec{r})(\mathbb{1}+iK)^{-1}_{l'l}\ , \tag{4.3}$$

where σ_l is the Coulomb phase shift appropriate to the momentum k, and $K_{ll'}$ are K-matrix elements. Then, using Eq. (4.3), the matrix elements $I_{lm\mu}$ are given by

$$I_{lm\mu}=k^{1/2}e^{i\sigma_l}\sum_{l'}\langle\phi\,|\,p_\mu\,|\,\psi^{(P)}_{kl'm}\rangle(\mathbb{1}+iK)^{-1}_{l'l}\ . \tag{4.4}$$

There are thus two possible approaches to computing $I_{lm\mu}$. The first would be to directly obtain variational approximations and corrections to Eq. (4.2), and the second would be to compute variational approximations and corrections to both $\langle\phi\,|\,p_\mu\,|\,\psi^{(P)}_{kl'm}\rangle$ and $K_{ll'}$ and then use Eq. (4.4). The main drawback of the direct approach is that it would require the use of complex arithmetic which would then at least double the necessary computational effort for each correction step compared to the use of real arithmetic. On the other hand, the use of Eq. (4.4), which only involves real arithmetic, also requires the computation of two different matrix elements. With the Padé-approximant correction method, if $\langle\phi\,|\,p_\mu\,|\,\psi^{(P)}_{kl'm}\rangle$ is computed using a variational functional of the form $M^{n}_{i,j+2}(p_\mu\phi,S_{l'})$ and the K-matrix elements are computed using $M^{n}_{i,j}(VS_{l'},S_l)$, then the effort needed to compute the corrections to $M^{n}_{i,j+2}(p_\mu\phi,S_{l'})$ alone is not much less than the work needed to compute the corrections to both matrix elements. Thus the use of Eq. (4.4) will still be approximately twice as fast as the use of Eq. (4.2) directly for each iteration needed. However, the convergence properties of these two approaches are different. We found that the use of Eq. (4.4) occasionally leads initially to irregular convergence of the Padé-approximant correction method. One example of this problem is the 18-eV calculation in the $5\sigma\rightarrow k\sigma$ channel whose results are given in Table II. This behavior is due to the different rates of convergence of the two matrix elements $\langle\phi\,|\,p_\mu\,|\,\psi^{(P)}_{kl'm}\rangle$ and $K_{l'l}$, which is especially pronounced when an eigenphase of the K matrix goes through $\pm\pi/2$ during the iterative procedure. In all cases studied, the Padé correction procedure settles down after a few iterations and then converges.

We also examined the use of Eq. (4.2). This approach gave much smoother convergence. However, the computational effort was still much greater than was needed using Eq. (4.4) even though the Eq. (4.2) approach took a few iterations less. Thus all the results presented here using the Padé-approximant method were obtained by separately variationally correcting the matrix elements $\langle\phi\,|\,p_\mu\,|\,\psi^{(P)}_{kl'm}\rangle$ and $K_{l'l}$ and then combining them using Eq. (4.4) to yield a variational estimate of $I_{lm\mu}$.

TABLE II. Comparison of Padé-approximant and iterative Schwinger (ISM) correction methods. Results for the $5\sigma\rightarrow k\sigma$ photoionization channel of CO. These calculations were performed as discussed in the text using the variational expressions given in Eqs. (3.15) and (3.16) and using the initial basis set given in Table I.

	$E=18$ eV[a]				$E=25$ eV			
	Cross Section (Mb)[b]		Eigenphase Sum		Cross Section (Mb)		Eigenphase Sum	
N[c]	Padé	ISM	Padé	ISM	Padé	ISM	Padé	ISM
0	4.11	4.11	0.88	0.88	4.86	4.86	0.83	0.83
1	11.95	2.67	0.84	0.84	4.59	4.63	0.89	0.89
2	3.84	3.98	1.00	0.82	4.61	4.61	0.89	0.89
3	3.83	3.66	1.00	0.96	4.61	4.61	0.89	0.89
4		3.81		0.98				
5		3.92		1.01				
6		3.81		1.01				
7		3.85		1.00				

[a] E is the photon energy assuming an ionization potential of 14.0 eV (Ref. 44).
[b] Dipole-length form of the photoionization cross section. Note that 1 Mb is 10^{-18} cm^2.
[c] N is either the order of the Padé approximant used to compute M_c (i.e., $[N/N]$) as defined in Eq. (2.26), or the iteration number as defined in Eq. (2.29) for the iterative Schwinger method.

In contrast to the Padé-approximant method, the iterative Schwinger method[5] required considerably more computational effort to develop separate iterative corrections for both $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ and $K_{l'l}$. Thus in the present paper, to implement the iterative Schwinger method we will employ the same approach that was used in earlier studies,[11–15] which constructs iterative variational approximations only to the K-matrix elements using a variational expression of the form $M^n_{ij}(VS_{l'},S_l)$. Then the variational approximations to $\langle \phi \mid p_\mu \mid \psi_{kl'm} \rangle$ are obtained using a variational expression of the form $M^{n+1}_{i,j+1}(p_\mu\phi,S_{l'})$ and the same basis set $A \cup C^N$ employed in Eq. (2.29), which is used to construct the iterative approximations of $K_{ll'}$.

To compute the 5σ photoionization cross section of CO, we have chosen to use the functionals $M^3_{3,5}(p_\mu\phi,S_{l'})$ and $M^2_{3,3}(VS_{l'},S_l)$, defined by Eqs. (3.16) and (3.15), to compute the matrix elements $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ and $K_{l'l}$. This choice was based upon the conclusion of the study of Lee *et al.*[6] that functionals of this form gave better results for the CO^+ system than do the corresponding Schwinger functionals $M^1_{13}(p_\mu\phi,S_{l'})$ and $M^0_{11}(VS_{l'},S_l)$ defined by Eqs. (3.14) and (3.13).

In computing the K matrix, we use the fact that $K_{ll'}$ is a square matrix and compute the whole matrix at one time rather than computing each matrix element individually. When using the Padé-approximant approach this implies that we use for the augmentation bases sets B^N_K a set of functions of the form

$$B^N_K=\{[(K+KTK)(1-P)]^j \mid \psi_{0,l_i} \rangle:\ j=1,2,\ldots,N-1 \text{ and } l_i=0,1,\ldots,l_p\} \tag{4.5}$$

with a similar expression for B^N_B. When this form of augmentation basis set is used the correction formed then corresponds to a matrix-Padé approximant to the matrix $M_{c,ll'}$.[2] Analogously, when the iterative Schwinger method is used one can write the augmentation basis set as

$$C^N_K=\{ \mid \psi^S_{N,l_i} \rangle:\ l_i=0,1,\ldots,l_p\} \tag{4.6}$$

with a similar expression for C^N_B. Then the convergence condition from Eq. (2.32a) becomes

$$D^{-1}_{ij}\langle v_j \mid S_{l_k} \rangle = \begin{cases} 1, & \text{for diagonal elements, i.e., } \mid u_i \rangle = \mid \psi^S_{N,l_k} \rangle \\ 0, & \text{otherwise} \end{cases} \tag{4.7}$$

with a similar expression for Eq. (2.32b). By using these matrix forms for the K-matrix calculations, we are using larger variational basis sets which should thus give more rapid convergence than using the correction procedures for each matrix element separately.

In contrast to the K matrix, the dipole matrix $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ is not, in general, a square matrix. As discussed in Sec. II we cannot construct variational approximations to $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ using bra and ket basis sets of different sizes. Therefore, when computing the variational corrections to $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ with the Padé approximants we cannot use the matrix-Padé approach as was possible for the K matrix, but we must calculate the variational Padé corrections for each matrix element $\langle \phi \mid p_\mu \mid \psi^{(P)}_{kl'm} \rangle$ individually.

C. Comparison of Padé-approximant and iterative Schwinger methods

In Table II we compare the results of the Padé-approximant and iterative Schwinger correction

TABLE III. Condition for correct convergence of the iterative Schwinger method. The matrix elements listed are the diagonal matrix elements of the matrix given in Eq. (4.7) and thus should converge to the value 1.00 to insure that the iterative Schwinger method has converged to the correct solution.

		$E=18$ eV		
N[a]	$l=0$[b]	1	2	3
1	0.86	−1.53	12.50	−11.89
2	0.96	0.96	1.02	1.04
3	0.91	0.06	3.81	−0.38
4	1.00	0.77	1.60	0.46
5	1.03	1.36	−0.36	2.69
6	0.99	0.95	1.30	0.67
7	1.00	1.04	0.82	1.18
		$E=25$ eV		
1	−0.38	1.16	1.63	1.24
2	−0.20	1.21	1.24	0.94
3	−0.14	1.18	1.28	1.02

[a]Iteration number of the iterative Schwinger method.
[b]l_k of the diagonal matrix element as given in Eq. (4.7).

methods for the $5\sigma \rightarrow k\sigma$ photoionization channel of CO. Naturally, the $N=0$ results are identical for these two methods, as are the $N=1$ results for the eigenphase sum. In Table III we examine how well the condition for proper convergence given in Eq. (4.7) is satisfied. These examples illustrate two types of problems occasionally encountered with the iterative Schwinger method. The first problem is that the iterative Schwinger approach can converge considerably more slowly at some energies than at others. This is clearly the case for the 18-eV calculation reported in Tables II and III, where seven iterations were required before the condition for proper convergence, Eq. (4.7), was well satisfied. A second feature of the iterative Schwinger method is illustrated by the 25-eV calculation where the cross section and eigenphase sums have converged to the correct values but the condition for proper convergence of the wave function is not satisfied. In this case, although the variational basis set C_K^N does not contain the exact solutions, which would have been the case if the procedure had properly converged, the fact that *variational* expressions were used to compute both $K_{ll'}$ and $\langle \phi \mid p_\mu \mid \psi_{kl'm}^{(P)} \rangle$ has led to only small errors in these matrix elements.

From Table II we see that the Padé-approximant correction procedure is well converged by the second iteration in both of these cases. For all further results presented here we will employ the Padé-approximant approach and we regard the calculation as converged when the photoionization cross sections (both dipole-length and dipole-velocity forms) change by less than 0.01 Mb between the $[(N-1)/(N-1)]$ and $[N/N]$ approximants. This convergence criterion was generally satisfied by computing approximants up to order [3/3] or [4/4].

D. Converged cross sections

In Figs. 1—3 we present the converged results for the photoionization of the 5σ level of CO. We compare the present results to other theoretical and to experimental data. The curves from the present study presented in these figures were obtained by computing the cross sections, using the Padé-approximant method discussed above, at the photon energies of 15, 18, 21, 23, 25, 27, 29, 32, 36, and 40 eV and interpolating these values to other energies. We take the ionization potential for 5σ photoionization of CO leading to the $X\,^2\Sigma^+$ state to be 14.0 eV.[44]

In Fig. 1 we compare the present results with the experimental data of Plummer *et al.*[34] obtained using synchrotron radiation and of Hammett *et al.*[33] from an $(e,2e)$ technique. We also compare the accurate FCHF results obtained here with the STMT

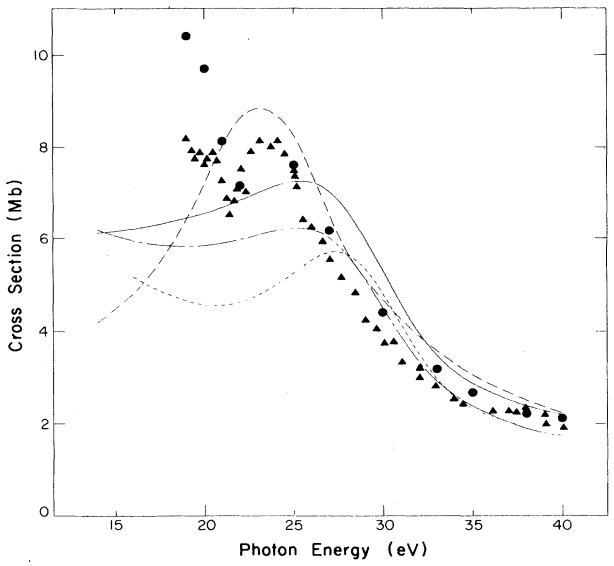

FIG. 1. Photoionization cross section for the production of the $X\,^2\Sigma^+(5\sigma)^{-1}$ state of CO^+: ——, present results using the dipole-length approximation; —·—·—, present results using the dipole-velocity approximation; ---, MSM results of Davenport (Ref. 29); ———, STMT results of Padial *et al.* (Ref. 32); ●, experimental results of Hamnett *et al.* (Ref. 33); ▲, experimental results of Plummer *et al.* (Ref. 34).

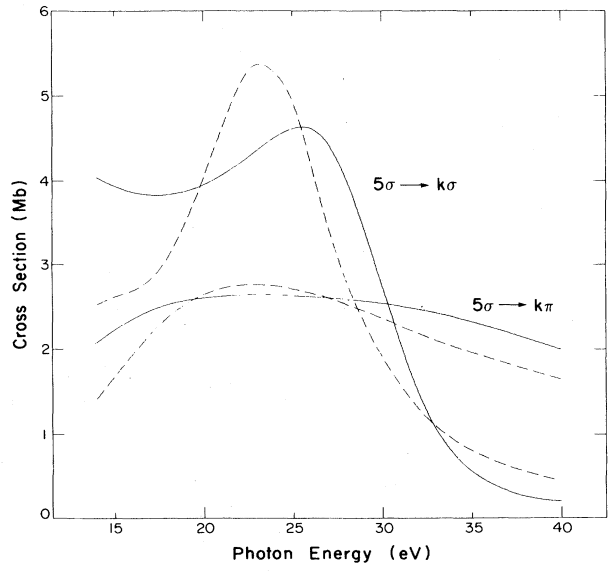

FIG. 2. Photoionization cross sections of CO in the $5\sigma \rightarrow k\sigma$ and $5\sigma \rightarrow k\pi$ channels using the frozen-core—Hartree-Fock and dipole-length approximations: ——, present results; ———, STMT results of Padial *et al.* (Ref. 32).

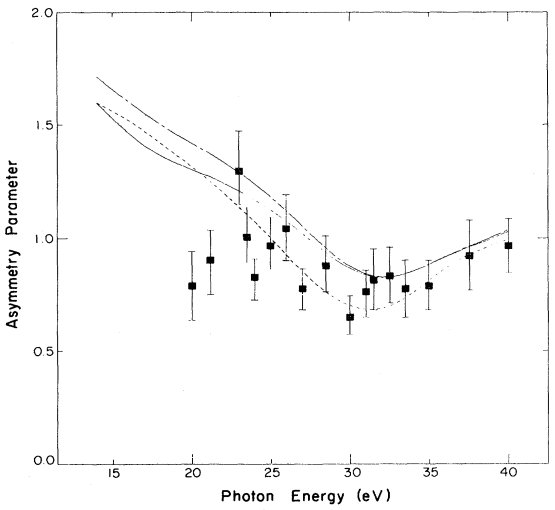

FIG. 3. Photoelectron asymmetry parameters for photoionization leading to the $X\,^2\Sigma^+(5\sigma)^{-1}$ state of CO^+: ——, present results using the dipole-length approximation; —·—·—, present results using the dipole-velocity approximation; ---, MSM results of Wallace *et al.* (Ref. 30); ■, experimental results of Marr *et al.* (Ref. 35).

results of Padial *et al.*[32] and with the MSM results of Davenport.[29]

We present, in Fig. 1, both the dipole-length and dipole-velocity forms of the cross section in the FCHF approximation. We have hence neglected electron correlation effects in both the initial and final states of the photoionization process. In our previous study of the photoionization of N_2 (Ref. 12) we considered initial-state correlation effects and found that in the $3\sigma_g$ channel of N_2, which is analogous to 5σ photoionization of CO, the effect of initial-state correlation in the region of the shape resonance was to lower the dipole-length cross section into good agreement with the dipole-velocity cross section which was not appreciably affected by the inclusion of initial-state correlation. By analogy one would expect that inclusion of initial-state correlation in the 5σ photoionization of CO would likewise lower the length cross section in the 20 to 30 eV energy range. Thus we expect that the major discrepancies between the present theoretical results and the experimental results in the energy region around 24 eV and below 21 eV are due to the neglect of autoionizing effects. The possible effects of autoionization on vibrational branching ratios in this region have recently been discussed by Stephens *et al.*[31] Besides these discrepancies, the underlying cross section seems to be well represented by the FCHF results presented here.

A comparison of our results with those of Davenport[29] obtained using the MSM approach show that the MSM results are in qualitative agreement with the present results (see Fig. 1). However, quantitative aspects such as the position of the resonance and the low-energy cross-sections are not accurately reproduced.[29]

The STMT results of Padial *et al.*,[32] in Fig. 1, are qualitatively different from either the present results or the MSM results of Davenport.[29] The STMT results, which were also obtained in the FCHF approximation using the dipole-length form, seem to indicate that the feature at 24 eV can be attributed to the effects of the shape resonance in the $5\sigma\rightarrow k\sigma$ channel, whereas the present results indicate that autoionization is important in this region. Moreover, the low-energy behavior of the STMT cross section is quite different from the present results. Some of these differences between the present results and those of the STMT method[32] may be due to the use of different Hartree-Fock target orbitals, i.e., a Slater basis in this work and a Cartesian Gaussian basis in the STMT calculations. We do not believe, however, that this will account for the principal discrepancies seen in these two sets of cross sections.

In Fig. 2 we give the individual channel contributions to the 5σ photoionization cross sections of CO in the present calculation and of the STMT calculations of Padial *et al.*[32] The STMT results for these two channels seem to oscillate about the accurate FCHF cross sections computed here. This type of behavior of the STMT photoionization cross sections, when compared to accurate FCHF results, has been observed in other molecular systems.[12,15] Although the $5\sigma\rightarrow k\pi$ cross section is fairly well represented by the STMT method, the $5\sigma\rightarrow k\sigma$ STMT cross section has a very different nonresonant background contribution.

Finally, in Fig. 3, we compare the photoelectron asymmetry parameter β computed in the present study, with the experimental data of Marr *et al.*[35] and with the calculated results of Wallace *et al.*[30] We see that the MSM asymmetry parameters agree quite well with the accurate FCHF results. Both the MSM and FCHF results are in fairly good agreement with the experimental results. In the regions where final-state correlation effects seem to be important in the total cross sections presented in Fig. 1, i.e., around 24 eV and below 21 eV, we see discrepancies between experiment and theory in the photoelectron angular distributions. Structure in the β parameters around 24 eV is probably also due to autoionization.[31] The broad minimum in the β's centered around the photon energy of 31 eV is well reproduced by the theories and is directly attributable to the $5\sigma\rightarrow k\sigma$ shape resonance which produces the peak in the cross section at 25 eV.

V. CONCLUSIONS

We have shown that the photoionization cross sections obtained using the iterative Schwinger method are variationally stable and thus, even when the wave function of the iterative Schwinger method is not completely converged, the computed cross sections can still be accurate. The Padé-approximant correction method discussed here has been found to be more rapidly and uniformly convergent than the iterative Schwinger method. We have also shown that the Padé-approximant method can be applied to a wide variety of variational expressions for matrix elements of the general form $\langle R \mid \psi \rangle$. The Padé-approximant method thus appears to be a promising approach to solving the single-center static-exchange equations for molecular systems.

In the theoretical study of molecular photoionization, it is important to obtain accurate Hartree-Fock level cross sections such as those given here. Converged Hartree-Fock cross sections, when compared with experimental data, clearly indicate in which spectral regions autoionization effects are important, and thus where more refined calculations are needed to fully understand the photoionization process. Also, accurate Hartree-Fock cross sections are needed so quantitative evaluations of other theoretical approaches can be made.

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